REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE** Technical Papers	**3. DATES COVERED** *(From - To)*
4. TITLE AND SUBTITLE Please see		**5a. CONTRACT NUMBER**
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) attached		**5d. PROJECT NUMBER** 1011
		5e. TASK NUMBER 0046
		5f. WORK UNIT NUMBER 346204
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048		**8. PERFORMING ORGANIZATION REPORT**
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048		**10. SPONSOR/MONITOR'S ACRONYM(S)**
		11. SPONSOR/MONITOR'S NUMBER(S) Please see attached

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

20030204 078

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Leilani Richardson
a. REPORT Unclassified	**b. ABSTRACT** Unclassified	**c. THIS PAGE** Unclassified	A		**19b. TELEPHONE NUMBER** *(include area code)* (661) 275-5015

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FROM: PROI (STINFO) 11 June 2001

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2001-137**
T. Hawkins, A. Brand, M. McKay, G. Drake, I.M.K. Ismail, "Characterization of Reduced Toxicity, High Performance Monopropellants at the U.S. Air Force Reearch Laboratory"

International Conference on Green Propellant for Space Propulsion **(Statement A)**
(Noordwijk, The Netherlands, 20 June 2001)(Deadline: 12 June 2001)

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Characterization of Reduced Toxicity, High Performance Monopropellants at the U.S. Air Force Research Laboratory*

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ABSTRACT

Current U.S. Air Force programs are aiming to develop reduced toxicity monopropellant formulations to replace spacecraft hydrazine monopropellant and exceed the monopropellant performance objective (> 50% increase in density impulse) specified by the Integrated High Payoff Rocket Propulsion Technology (IHPRPT) Program. The creation of such monopropellants can offer considerable cost savings associated with the handling and loading of propellants, longer spacecraft service life, smaller vehicle design, or heavier payloads.

The Air Force Research Laboratory (AFRL) approach to replacing hydrazine is the development of energetic liquid salt mixtures with substantially less vapor toxicity and superior performance (specific impulse and density). These liquid salt mixtures show promise as one avenue toward replacement of hydrazine monopropellant. During the last year, work has centered on the production and characterization of a few of these reduced toxicity monopropellant formulations. Limited safety and sensitivity, thermal stability, rheology and toxicity studies have been conducted. Also, thruster testing of selected propellants has been performed. The results of these efforts will be presented.

INTRODUCTION

Due at least partially to the simplicity of system design, monopropellant system development has been a subject of propulsion research for quite some time. During the 1940s and 1950s, efforts focused on evaluations of monopropellants such as hydrogen peroxide, propyl nitrate, ethylene oxide and hydrazine. The NASA Jet Propulsion Laboratory (JPL) championed the use of hydrazine in Voyager in the 1970s, and hydrazine has subsequently become the monopropellant of choice for small engines of spacecraft in attitude, on-orbit maneuvering and gas generator applications.[1]

The high vapor toxicity and vapor pressure of hydrazine, coupled with the desire to significantly increase the density impulse, present significant technical challenges to be overcome in producing next-generation monopropellants. The approach taken by the Air Force Research Laboratory is the use of energetic ionic compounds to replace hydrazine. In the past, such efforts often attempted to produce low melting point salt mixtures containing toxic hydrazines and amines as melt point depressants.[2] JPL, the Naval Ordnance Testing Station, Naval Research Laboratory and other laboratories have examined such mixtures of salts and solvents since the 1950s. This work arose from efforts to find a hydrazine replacement with a significantly lower melting point. Typically, mixtures of hydrazine with its salts tended to be too detonable. Also, the British examined mixtures of ammonium nitrate, a fuel and water. Such compositions usually suffered from poor performance.[2]

The AFRL effort expressly focuses on identification of high concentration salt compositions that are virtually free of toxic vapor and possess significant improvement in performance. Basic research work at AFRL is directed toward producing novel energetic salts for monopropellant. (This work is sponsored, in

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part, by the U.S. Air Force Office of Scientific Research.) Such ionic compounds can be produced which yield low melting point, liquid mixtures. The coulombic attraction of these ions acts to tightly hold them in the liquid phase and consequently reduces any risk of toxicity posed by the vapor of the monopropellant. This mechanism of vapor pressure reduction has been generally recognized for ionic liquids.[3]

Aside from a low melting point and toxicity, there are a number of properties that are desirable for a monopropellant successor to hydrazine. Table 1 outlines nine objectives to be met for an acceptable monopropellant. This listing should not be taken as comprehensive, however. Property requirements are mission dependent and can entail more exacting criteria. Other characteristics which are also important to consider for propellant evaluation and use include vapor pressure, viscosity as a function of shear rate and temperature, surface tension, compatibility with structural materials, propellant cost, ignitability, combustion temperature and combustion behavior over the applicable engine chamber pressure range.

Table 1. Desirable Monopropellant Properties

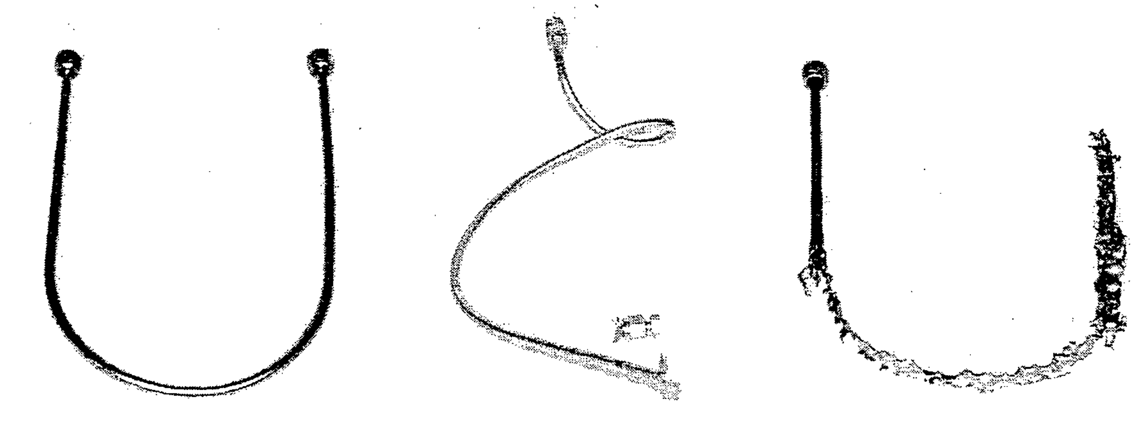
Characteristic	**Objective**
Density Isp [2.07 MPa-vac; exp=50]	$> 3.53 \cdot 10^5$ kg-sec/m^3 (12.7 lb-sec/in^3)
Vapor toxicity	Does not exceed TLV (No SCBA in handling)
Carbon content	No solid carbon forms in theoretical exhaust
Melting point	$< 2^oC$
Detonability [NOL card gap]	Class 1.3; (Prefer 24 cards maximum (E_{50}))
Impact sensitivity [drop weight]	20 kg-cm minimum (E_{50})
Adiabatic compression [U-Tube test]	No explosive decomposition (Pressure ratio of 35)
Thermal stability	< 2% by wt. decomposition for 48 hrs at 75 ^oC
Critical diameter	No propagation in lines of < 1.91-cm diameter

This report constitutes a summary of the ongoing propellant development effort. A monopropellant (denoted as AFN1) was formulated that was representative of the compositions under investigation, and it was characterized for stability, physical properties, toxicity, and performance. Property comparisons are made with the state-of-the-art propellant, hydrazine.

EXPERIMENTAL

Adiabatic Compressibility Tests - An apparatus for estimating the sensitivity of propellant materials towards mechanical shocks (Adiabatic Compression Tester) was constructed at AFRL. A propellant sample is placed into a 316 stainless steel U-tube and held at a temperature that is set between 20 and 150°C. The sample is then exposed to an abrupt mechanical shock produced by the rapid introduction of nitrogen gas into the tube at a pressure between 3.45 and 20.7 MPa (500 to 3000 psi). A pressurization rate of 827 MPa/sec (120,000 psi/sec) was measured for the apparatus operated at 3000 psi driving pressure. The apparatus is computer interfaced and is driven with LABTECH NOTEBOOK-pro™ Software. For the tests conducted in this report, the propellant was equilibrated to 20°C and the nitrogen pressure was 3.45 MPa for a driving pressure ratio of 35/1. A positive reaction of the propellant to adiabatic compression results in a highly deformed and fragmented U-tube. (Figure 1 depicts positive and negative results from compression testing.) Tests were performed in triplicate and hydrazine was employed as a test control.

Detonability Tests - A test rig was designed and assembled for the detonability assessments (see Figure 2). The test rig consists of a 0.635-cm, inner diameter stainless steel pipe (the container of the propellant) that rests upon a mild steel witness plate of 0.098-cm thickness. A C-4 booster (L/D of 1) with detonator cap rest on top of the containment pipe that is filled with propellant. The pipe (L/D of 8) is fitted with a line of piezoelectric crystalline pins accurately spaced along its length and attached to a high-speed recording oscilloscope. After detonation of the booster charge, the velocity of the shock wave through the propellant is assessed by reducing the oscilloscope data. Also, the witness plate is examined to determine whether the propellant sustained a detonation through the length of the containment pipe. The testing of trimethylolethanetrinitrate (TMETN) was performed as a control.



(a) New tube or negative test (b) Ruptured- positive test (c) Severely damaged tube-positive test

FIGURE 1. Positive and Negative Adiabatic Compression Test Results

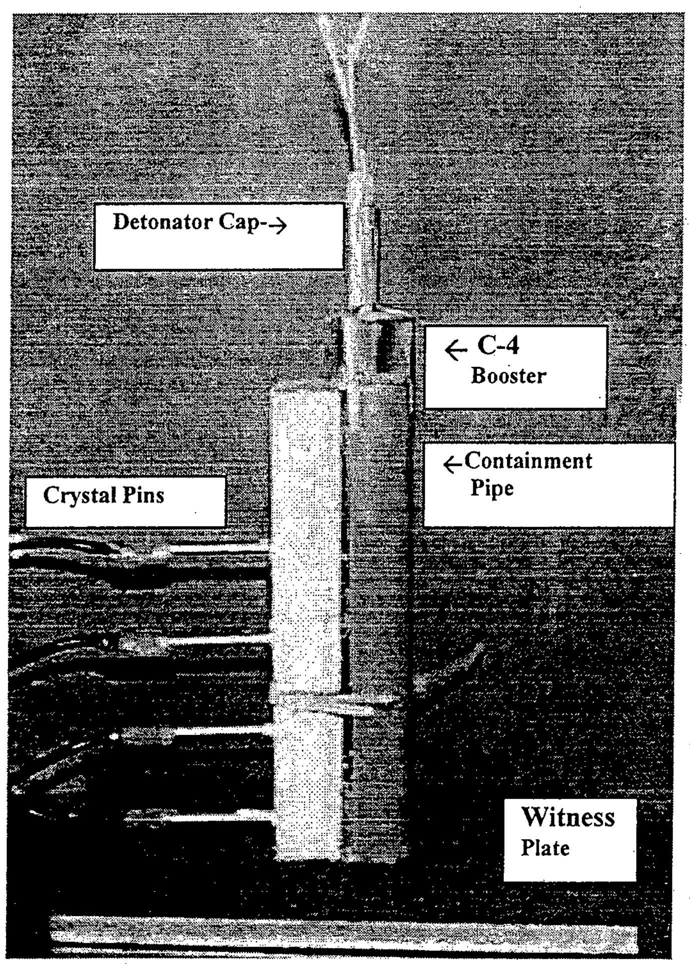


FIGURE 2. Specimen for 1.91-cm Diameter, Confined Detonation Propagation Test

Thruster Tests - To demonstrate the feasibility of candidate monopropellant formulations, a robust modular monopropellant thruster is employed. The hardware consists of a stainless steel foreclosure, case, and an aft-closure containing a nozzle with a graphite insert. The fore-closure accommodates a monopropellant feed line leading directly into a 120-degree full-cone spray nozzle, and contains mounting hardware to fix the thruster vertically on a thrust stand. The 5.1-cm (diameter) by 10.2-cm (length) stainless steel case accommodates a pressure transducer and two thermocouples (for measurement of chamber and catalyst bed temperature). The thrust capability and L/D ratio were adapted by varying the thickness of steel cylindrical inserts that were pressure fitted into the case. A catalyst bed was incorporated with the same diameter as that of the bore of the selected case insert. Finally, the graphite nozzle was held in place by the aft-closure and a retainer ring. Table 2 depicts design parameters that are typical of the thrusters employed in this work.

Thruster firings are conducted using a test stand with a 1-liter feed tank capable of being pressurized to 10.3 Mpa (1500 psi) and placed on a digital balance used to record weight loss (mass flow rate). A turbine flow meter is placed in line to measure volumetric flow. A solenoid valve placed just upstream of the thruster controls the duration of monopropellant flow. Instrumentation to the entire system collects data on the feed tank pressure, turbine flow meter, line pressure upstream of the solenoid valve, duration the solenoid valve is open, temperatures of the thruster catalyst bed and chamber, the chamber pressure, and the resulting thrust. This instrumentation design allows for redundant measurements on the monopropellant flow rate and calculation of the system pressure drop.

Table 2. Thruster Design Parameters

Chamber volume	**51.8 cm^3**
Chamber L/D	**4**
Chamber length	**10.2 cm**
Chamber diameter	**2.54 cm**
Nozzle throat diameter	**0.536 cm**
Nozzle throat area	**0.023 cm^2**
Nozzle exit diameter	**1.05 cm**
Nozzle exit area	**0.858 cm^2**
Catalyst bed volume	**19.3 cm^3**
Catalyst bed length	**3.81 cm**
Catalyst bed diameter	**2.54 cm**
Catalyst weight	**27.0 g**
Thrust (at P_C=2.07 MPa)	**67 N (est.)**

A catalytic method was chosen for ignition of monopropellant. A relatively rapid decomposition rate at elevated temperatures was fortunately observed with Shell 405 catalyst (iridium coated alumina catalyst used commercially for hydrazine) for the developmental monopropellant. Although the combustion temperature of the high performance, developmental monopropellant is unacceptably high for maintaining the integrity of the catalyst after repeated firings, catalytic ignition was deemed sufficient for test and evaluation purposes.

The catalyst bed is a 2.54-cm (diameter) x 3.81-cm (length) steel cylinder with 40-mesh molybdenum wire screen on either end to contain 25-30 mesh Shell 405 catalyst. A 0.64-cm perforated Inconel or TZM alloy plate with 37 holes of 0.25-cm diameter supports the bed. The bed typically contains approximately 20 grams of fine catalyst (25-30 mesh) with approximately 7 grams of coarse (14x18 mesh) Shell 405 placed in the bed upstream of the support plate and separated by a molybdenum screen to help minimize the

pressure drop and prevent ejection of the finer catalyst through the holes of the support plate. The trade-off for using coarser catalyst however is a loss in some catalytic surface area. Also, to aid ignition, heat tape is wrapped around the thruster and testing is initiated once the catalyst bed temperature reaches 204°C. (It is standard practice to heat the catalyst beds in spacecraft thrusters.)

Thruster tests of the monopropellants (AFN1 and hydrazine) were executed by performing a series of six firings of each propellant. Typically an initial 0.5-sec pulse was applied to clear the dead space in the propellant feedline upstream of the solenoid valve leading to the thruster. (This also acts to further heat the catalyst bed for subsequent tests.) The following tests were generally conducted with 2.0-2.5-sec pulse duration. Depending on the propellant, the chamber pressure attained steady state within approximately 40-150 msec. Steady state values for chamber pressure were obtained by data averaging techniques (test stand ringing and noise were present in all firings).

RESULTS AND DISCUSSION

Theoretical Performance - AFN1 monopropellant has superior theoretical specific impulse and density to that of hydrazine (see Table 3). Also, the propellant's volumetric impulse of $3.81 \cdot 10^5$ kg-sec/m^3 (13.7 lb-sec/in^3) surpasses the objective of $3.53 \cdot 10^5$ kg-sec/m^3 (12.7 lb-sec/in^3) given in Table 1.

Table 3. Monopropellant Properties

Properties	**AFN1**	**Hydrazine**
Isp, sec; (a)	261	233
Density , g/cc	1.46	1.01
Chamber temp. (Theoretical) , K	2083	883
Carbon content of exhaust; (b)	none	none
Impact sensitivity*, kg-cm (5 negatives)	60	>200
Friction sensitivity, N (5 negatives)	300	>371
NOL card gap (at 69 Cards)	negative	negative
Thermal stability, %wt loss/48hr,75°C	1.96	(< 0.1)
Melt point, °C	<-22	1

a: Theoretical, calculated with 2.07 MPa (300 psi) chamber pressure, exhaust to vacuum, 50/1 expansion
b: as soot or solid carbon (by theoretical computation)
*: For reference, n-propylnitrate had an impact sensitivity of 8 kg-cm

Friction and Impact Sensitivity Properties - In regard to friction sensitivity the propellant is relatively insensitive- only showing positive reaction near the highest setting of the Julius Peters Testing equipment. The Olin-Mathieson impact sensitivity of the developmental propellant is similar to the impact insensitivity of hydrazine. AFN1 does display some impact sensitivity, but it is considerably less sensitive than a primary nitrate ester (i.e., n-propyl nitrate). All the measured properties of the developmental propellant meet the objectives in Table 1.

Adiabatic Compressibility Tests - Adiabatic compressibility tests were successfully performed in triplicate on the AFN1 monopropellant. The propellant displayed no reaction (no U-tube deformation) at a driving pressure ratio of 35/1 at 20°C. The test on hydrazine conducted by AFRL also resulted in a negative response. Consequently, AFN1 displayed insensitivity on par with hydrazine at the driving pressure ratio and temperature conditions of the measurements.

Detonability Tests - The AFN1 monopropellant was first evaluated by NOL card gap test. The propellant was found to exhibit class 1.3 detonability (negative results in the NOL card gap test at 69 cards). Next, the test for detonation propagation in a confined, 1.9-cm (0.75-in) pipe was conducted successfully, and the witness plates showed no detonation was propagated in the case of the AFN1 propellant. The test conducted with TMETN demonstrated a positive indication of detonation (i.e., a hole was cleanly cut through the witness plate).

The velocity of the pressure wave through the test propellants was determined and compared to the theoretical detonation velocity as computed from CHEETAH code[4]. Table 4 shows the resulting data. The experimentally determined velocity of the AFN1 monopropellant decayed with distance from the booster and is significantly less than the expected (theoretically determined) detonation velocity. The theoretical velocity for TMETN closely matched the experimental velocity.

Thus, the current effort has shown the AFN1 propellant possesses a confined, critical diameter greater than 1.9-cm. This propellant meets the critical diameter requirement generally applied to monopropellants.

Table 4. Experimental and Theoretical Shock Velocities for Monopropellants

Propellant	Theoretical Detonation Velocity (km/s)	Experimental Velocity (km/s)
AFN1	6.85	2.1
TMETN	7.19	7.1

Rheology - The rheology of a liquid propellant is an important characteristic and significantly impacts the operational range and design of the thruster. Liquids with higher viscosity naturally produce higher pressure drops through fuel lines than lower viscosity liquids (all else being equal). Thus, higher head pressures are required for engine operation. This situation dictates that a viscosity threshold exists which makes employment of a monopropellant impractical when its viscosity exceeds that threshold. Also, extreme variation of viscosity, over the operational range of the thruster, is to be avoided. Extreme variations create difficulty in maintaining consistent thrust profiles throughout the range of operational environments. The allowable viscosity ranges and thresholds will depend on the particular thruster design and the constraints placed upon it; however, the general desire is obviously to employ a monopropellant with as low a viscosity as possible and, ideally, with no variation in viscosity with temperature.

At 23°C the viscosity of AFN1 was measured at 0.0231 Pa-sec. This viscosity was well within the operable range for the thruster employed in our program. As temperature is lowered and approaches 0°C hydrazine becomes essentially unusable due to phase changes and solidification. AFN1 rises in viscosity as temperature decreases, but remains liquid below 0°C. The utility of AFN1 at temperatures at or below 0°C may certainly be an issue, and is best addressed through engineering analysis of specific propulsion system designs.

Thruster Performance - A comparison of the performance of the developmental monopropellants in thruster tests is given in Table 5. The characteristic exhaust velocity, C^*, is a function of the monopropellant (the combustion temperature and properties of the exhaust species) and independent of the nozzle design.[5] The C^* efficiency measured for AFN1 is similar to that of hydrazine (i.e., C^*=95%). Scanning electron microscopic analysis of the catalyst before and after the firing showed the catalyst surface to have been severely damaged (sintered).

It is reasonable to expect that, with improvement in combustion chamber design, the propellant performance should be increased. The C^* efficiency measurement made on the developmental propellant

indicates that one can also reasonably expect to attain the density impulse improvements over hydrazine which are sought (see Table 1) for next generation, low-toxicity monopropellants.

Table 5. Thruster Test Results For Monopropellants

TEST PARAMETERS	AFN1	Hydrazine*
C* , theoretical (m/sec)	1373	1313
C* , measured (m/sec)	1309	1259
C* efficiency (%)	95.3	95.8
Chamber pressure (MPa)	1.45	2.07
Throughput (L/sec-m^2)	34.2	74.7
Pulse duration (sec)	2.00	2.50

* Catalytic decomposition at 64% ammonia dissociation

Monopropellant Toxicity – Toxicological tests of the ingredients comprising AFN1 were conducted by the Toxicology Division at Wright-Patterson AFB. These test results can be used to give an estimate of the toxicity of AFN1. The results in Table 6 compare the median lethal dosage (LD50), dermal reaction and genotoxicity estimates for AFN1 with hydrazine. Hydrazine has a lower lethal dosage than that for AFN1. With respect to dermal reaction, AFN1 is found to be much less irritating than hydrazine The genotoxicity evaluations showed hydrazine as strongly positive (as expected). AFN1 is found to have some effect on two of the five salmonella strains used in the test. It is important to recall that the Ames test evaluates the genotoxicity of propellant molecules in the liquid phase, and that the vapor concentration of such molecules is essentially nil for AFN1. Consequently, gloves and face shield are recommended in handling AFN1, but no SCBA is required (in contrast to the requirement for hydrazine).

Table 6. Toxicological Properties of Monopropellant Ingredients

PROPERTY	AFN1	HYDRAZINE
LD50 (rat), mg/kg	325-367	60
Dermal Irritation	Slight-Moderate	Corrosive
Genotoxicity (Ames)	3 Negative/ 2 Positive	Positive

It is expected that, as the development program progresses, additional toxicological testing will be performed. This includes dermal LD50, aerosol inhalation LD50 and eye irritation evaluations.

CONCLUSIONS AND RECOMMENDATIONS

While the monopropellant development program is an ongoing effort, several conclusions may be drawn from the work conducted. First, reduced toxicity monopropellants may be produced which meet given IHPRPT density impulse, thermal stability and safety/sensitivity objectives.

It should be noted that, while significant effort has been directed to evaluation of developmental monopropellants, additional testing must be performed to fully assess their properties. Characteristics to be addressed include surface tension, chemical compatibility with structural materials, additional toxicological evaluations, and combustion behavior over the applicable engine chamber pressure range. Moreover, additional effort is required in development of ignition methods that are compatible with the chemistry and temperature of combustion gases produced from the advanced monopropellants. High combustion temperatures (> 2000 K) render conventional catalysts useless for propulsion systems that require high

reliability and high reusability. Consequently, work in this area is desirable and currently being addressed at AFRL.

Finally, it is believed that stable monopropellants with significantly higher performance than that demonstrated in this report can be produced. Effort in synthesis of higher energy ingredients is underway and aimed specifically at allowing production of these higher performance propellants.

ACKNOWLEDGEMENTS

The authors thank Mr. Christopher Cass and the very capable crew of the National Hover Test Facility at AFRL for their commitment in the performance of the thruster tests. We also appreciate the support of Dr. Wesley Hoffman, Mr. Ronald Dettling, and Mr. Paul Jones for their help in propellant and materials test and evaluation. Thanks are also given to Dr. David Mattie of the AFRL Toxicology Group for his efforts in elucidating the toxicology of our propellants.

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